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Effect of torrefaction on structure and fast pyrolysis behavior of corncobs

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HIGHLIGHTS

- Torrefaction as pretreatment prior to fast pyrolysis can improve bio-oil quality.
- The structure change of torrefied corncob was quantitatively characterized by ^{13}C NMR.
- Bio-oil yield penalties were attributed to cross-linking and charring of corncobs.

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ABSTRACT

Pretreatment of corncobs using torrefaction was conducted in an auger reactor at 250–300 °C and residence times of 10–60 min. The torrefied corncobs were fast pyrolyzed in a bubbling fluidized bed reactor at 470 °C to obtain high-quality bio-oil. The heating value and pH of the bio-oil improved when the torrefaction as pretreatment was applied; however, increasing bio-oil yield penalties were observed with increasing torrefaction severity. Fourier transform infrared Spectroscopy (FTIR) and quantitative solid ^{13}C nuclear magnetic resonance spectrometry (NMR) analysis of torrefied corncobs showed that the devolatilization, crosslinking and charring of corncobs during torrefaction could be responsible for the bio-oil yield penalties. Gas chromatography-mass spectrometry (GC–MS) analysis showed that the acetic acid and furfural contents of the bio-oil decreased with torrefaction temperature or residence time. The results showed that torrefaction is an effective method of pretreatment for improving bio-oil quality if the crosslinking and charring of biomass can be restricted.

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1. Introduction

Biomass is the only renewable energy source that can be used as an alternative to fossil fuel for producing liquid fuel. Moreover, biomass conversion is considered as being environmentally friendly since it has a negligible sulfur, nitrogen, and metal content and is CO_2 neutral (Sharma and Bakhshi, 1993). Several processes are being studied to convert solid biomass into liquid fuel, including fermentation of biomass to ethanol, biomass gasification followed by Fischer–Tropsch or methanol synthesis, and aqueous phase reforming and so on (Carlson et al., 2008; Zhang et al., 2012). In comparison to these processes, fast pyrolysis of biomass provides for the highest yield of liquid products (as high as 70–80 wt.%) and lowest cost (Vispute et al., 2010; Zheng et al., 2012). Biomass fast pyrolysis is a thermal decomposition process that occurs in an inert atmosphere using high heating rates (10^3–10^4 K/s) and short residence times (<2 s) at about 450–550 °C to maximize liquid production with solid char and non-condensable gas as low yield co-products (Bridgwater, 1999; Garcia-Perez et al., 2008b). The liquid products, known as bio-oil, are a low-quality fuel that has a complex composition, high acid and high water contents, low heating value and storage instability (Czernik and Bridgwater, 2004; Mohan et al., 2006). Pretreatment of biomass prior to fast pyrolysis has been identified as one of the most promising methods to improve the quality of bio-oil (de Wild et al., 2009b; Meng et al., 2012).

Biomass has a complex composition, mainly comprised of hemicellulose, cellulose, lignin, extractives (tannins, fatty acids, resins), and ash. Pretreatment can alter the composition and structure of biomass leading to a change in the mechanism and product distribution of biomass fast pyrolysis (Hassan et al., 2009). Several pretreatment methods prior to fast pyrolysis have been investigated, including water leaching, pretreatment with dilute acid and alkali, and hot compressed water treatment. Water leaching removes alkali metals and alkaline earth metals, thus inhibiting their catalytic function during fast pyrolysis, resulting in a high yield of levoglucosan (Scott et al., 2001). Pretreatment with dilute acid and hot compressed water treatment can cause decomposition of hemicellulose, a decrease in the degree of polymerization (DP) and crystallinity of cellulose, resulting in a high yield of anhydrosugar (Chaiwat et al., 2008; de Wild et al., 2009b; Dobele et al., 1999). Pretreatment with dilute alkali can lead to the solubilization of hemicellulose and the disruption of the lignin structure (Alvira

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et al., 2010; Misson et al., 2009; Wang et al., 2011b). In addition to these methods, torrefaction can also been considered as a potential pretreatment prior to fast pyrolysis of biomass (Meng et al., 2012; Zheng et al., 2012). Torrefaction is a low-temperature pyrolysis process carried out at the temperature ranging from 200 to 300 °C to liberate water and release volatile organic compounds, primarily through the devolatilization of the hemicelluloses (de Wild et al., 2009a; Prins et al., 2006a). Torrefaction is an effective method to reduce the water, acid and oxygen contents of bio-oil to improve its heating value and pH (Meng et al., 2012; Zheng et al., 2012); however, the effects of torrefaction severity on the structure of torrefied biomass and its corresponding fast pyrolysis behavior, and especially the pyrolysis mechanism are currently not well understood. In the present study, torrefaction of corncobs was conducted in an auger reactor at 250, 275 and 300 °C and residence time of 10, 20 and 60 min. The torrefied corncobs were fast pyrolyzed in a bubbling fluidized bed reactor at 470 °C to obtain bio-oil. Solid ^{13}C NMR and FTIR were used to characterize the structural changes of the torrefied corncobs. The compositional analysis of the bio-oil was performed with GC–MS. The effects of torrefaction temperature and residence time on the change in fast pyrolysis behavior of torrefied corncobs are described and discussed and a mechanism is proposed.

2. Experimental

2.1. Preparation of torrefied corncob

Corncob was provided by the Baodi feed mill in Tianjin, China. The corncobs were ground, sieved to a particle size range of 0.25–0.40 mm, and dried at 105 °C for 8 h before torrefaction. The ultimate analysis and chemical composition analysis of corncob are shown in Table 1. The elemental analysis of corncob was performed on a Vario EL (Elementar Analysensysteme, Hanau, Germany). The chemical composition of the corncobs was analyzed according to the standard Laboratory Analytical Procedures (LAP) for "Determination of Structural Carbohydrates and Lignin in Biomass" provided by the National Renewable Energy Laboratory (NREL).

Torrefied corncobs were prepared in an auger reactor system. The schematic of the system is given in Fig. 1(a). The auger reactor was 100 mm in diameter and 0.6 m in length, and heated by an 3.5 kW electrical furnace. Temperature was controlled by a temperature control unit. The reaction temperature was set to 250, 275, or 300 °C, while the residence time was 20 min. The reaction residence time were controlled with a motor to maintain 10, 20 or 60 min when the reaction temperature was kept constant at 275 °C. Nitrogen flow was used to maintain an inert atmosphere and to remove volatile products from the reactor. The corncobs were moved through the heating reactor by the action of a rotating screw to obtain solid and volatile products. The solid products, known as torrefied corncobs, were collected in a collection bin. Each experiment was repeated twice under the same conditions.

2.2. Fast pyrolysis of torrefied corncob

Fast pyrolysis of torrefied corncobs was conduct in a 10 kg/h fluidized bed reactor system. The schematic of the system is shown in Fig. 1(b). It consisted of a gas pre-heater, screw feeder, fluidized bed reactor, two gas–solid cyclones, heat exchanger, two gas–liquid cyclones and cotton filter. The fluidized bed was 219 mm in diameter. Silica sand was used as bed material and to a height of 12 cm. Nitrogen was used as fluidizing gas at a flow rate of 12 Nm^3/h. The reaction temperature was 470 °C. The char was separated and collected by two gas–solid cyclones in series. These cyclones were maintained at 300 °C with heating tapes. The bio-oil was cooled and collected in a heat exchanger maintained at around −10 °C followed by two gas–liquid cyclones. The uncollected aerosol was absorbed by a cotton filter at the end of the system. Total liquid products included the liquid collected by heat exchanger, gas–liquid cyclones and weight gained by the cotton filter. The char products involved the char collected by two gas–solid cyclones and char in bed material. The char in the bed material was determined by oxidation at 650 °C for 5 h in a muffle furnace and measuring the weight loss. Each experiment was performed twice under the same conditions.

2.3. Characterization of torrefied corncob and bio-oil

The ^{13}C solid NMR spectra of torrefied corncobs, using a combination of cross-polarization (CP), magic angle sample spinning (MAS) and high-power proton decoupling, were obtained on a Bruker AV-300 solid NMR spectrometer operating at a proton frequency of 300 MHz (carbon frequency at 75 MHz) at room temperature. Acquisition was performed with a CP pulse sequence using a 2 ms proton 90° pulse of 2.4 μs. The MAS speed was 10.5 kHz, and the relaxation delay was 5 s. The solid ^{13}C CP/MAS NMR can be employed to obtain high-resolution solid NMR spectra in acceptable time consumed. However, one of the major drawbacks of CP/MAS NMR is that the present technique cannot be applied to directly obtain quantitative results. Two obstacles should be overcome prior to quantitative analysis using CP/MAS NMR. One is the overlapping of signals in spectra. Another one is that different carbons in spectra have different cross-polarization dynamic. Hence, in order to obtain quantitative results from the CP/MAS NMR experiments, all the signals in spectra were deconvolved into individual lines using Gaussian–Lorentzian fitting prior to integration. And then all the integrals were corrected by a factor taking into account the cross-polarization dynamics, which obtained by variable contact-time experiments according to literature works (Davis et al., 1994; Kolodziejski and Klinowski, 2002).

The Fourier transform infrared Spectroscopy (FTIR) analyses of torrefied corncobs were carried out on a Bruker TENSOR27 in order to characterize the main functional groups of the torrefied corncobs. KBr discs were prepared by mixing about 2 mg of sample with 200 mg of KBr.

The GC–MS analysis of bio-oil obtained from fast pyrolysis was performed on a Agilent 7890 GC followed by an Agilent 5973 mass selective detector (MSD). The GC column used was an HP-INNO-Wax column (30 m × 0.25 mm, 0.25 μm film thickness). The oven was programmed to hold at 50 °C for 2 min, then increased at 10 °C/min to 90 °C, followed by an increase at 4 °C/min to 120 °C, and an increased at 8 °C/min to 230 °C and holding there for 10 min. Helium was used as carrier gas. The injector temperature was 250 °C. The injector split ratio was set at 20:1. The ion source temperature was 240 °C for the mass spectrometer detector. The

Table 1
Ultimate analysis and chemical component analysis of corncob.

Sample	Ultimate analysis/wt.%, daf[a]					Chemical component analysis/wt.%			
	C	H	O[b]	N	S	Extractive	Hemicellulose	Cellulose	Lignin
Corncob	43.87	6.06	49.50	0.53	0.04	8.10	33.31	36.26	13.51

[a] daf: Dry ash free basis.

[b] The oxygen content was calculated by difference.

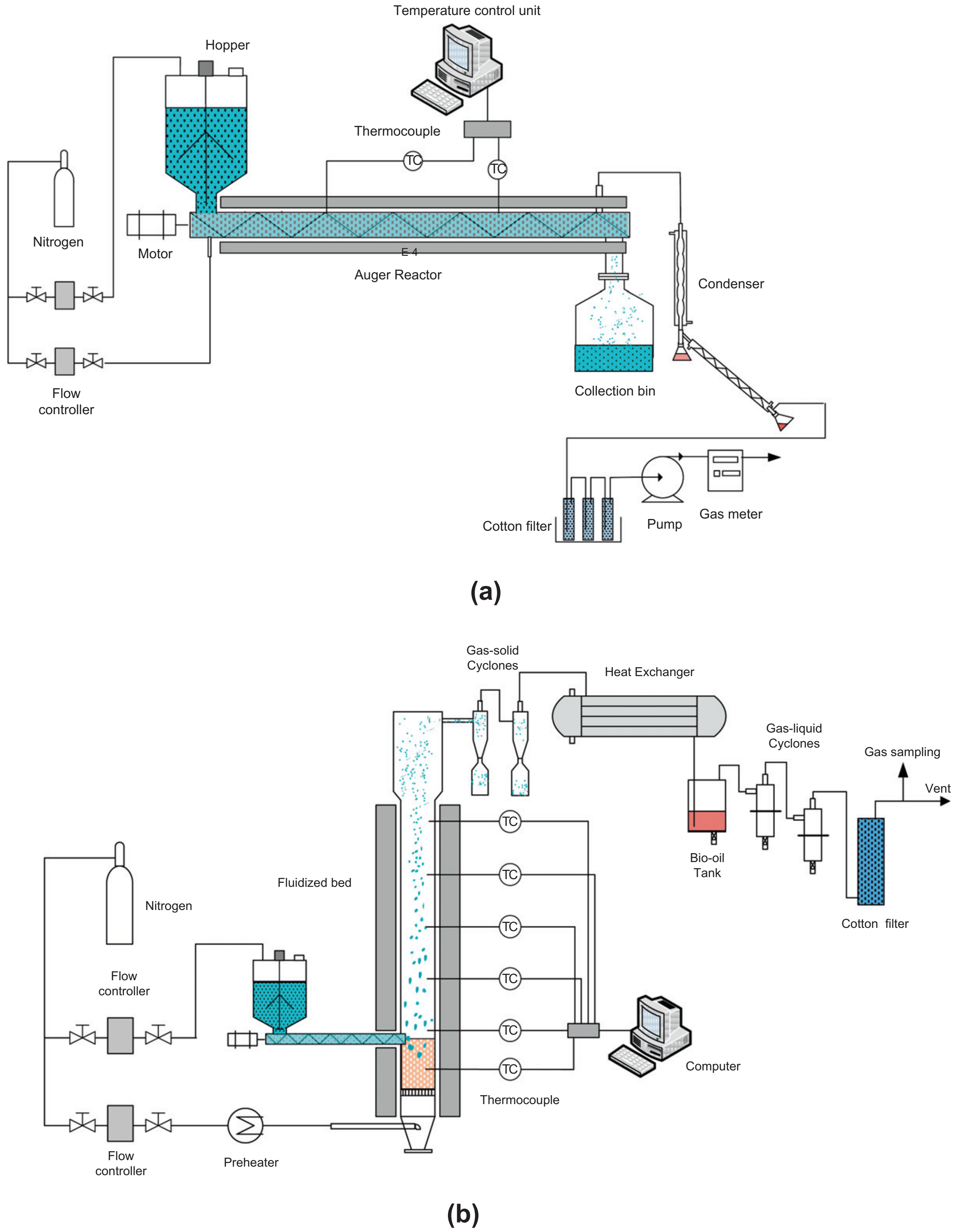

Fig. 1. Schemtic of experimental apparatus: (a) torrefaction system (b) fast pyrolysis system.

mass spectrometer was set at an ionizing voltage of 70 eV with a mass range (m/z) of 33–500 u. Compounds were identified by comparison with entries in the NIST mass spectral data library, and their response factors for GC quantification were determined using the external standard method.

The water content of bio-oil was analyzed by Karl Fischer titrimetry (787KF Titrino, Metrohm). The higher heating value of bio-oil was determined using an isoperibol oxygen bomb calorimeter (WZR-IT-C, BTYQ, Changsha). The pH of bio-oil was analyzed by a pH meter (PHS-3C, SPSIC, Shanghai). The dynamic viscosity was determined using viscometer (WYF108, Wuzhou, Dalian) at 20 °C. Each test was repeated three times under the same conditions. The reported data are the average of the three test results.

2.4. Data processing

The yield of bio-oil, char, non-condensable gas and the crystallinity of cellulose was defined as follows:

$$\text{Yield of bio}-\text{oil} = \frac{\text{mass of bio}-\text{oil}}{\text{mass of torrefied corncob}} \times 100\%$$
$$\text{Yield of char} = \frac{\text{mass of char}}{\text{mass of torrefied corncob}} \times 100\%$$
$$\text{Yield of non}-\text{condensable gas} = 100\% - \text{Yield of bio}-\text{oil} - \text{Yield of char}$$

$$\text{The crystallinity of cellulose} = \frac{\text{A88.1}}{\text{A88.1} + \text{A82.6}} \times 100\%,$$

where A88.1 and A82.6 are the normalized integration values in a deconvoluted spectrum corresponding to crystalline and amorphous C-4 cellulose regions(as shown in Fig. 2 and Table 3), respectively.

3. Results and discussion

3.1. Characterization of torrefied corncobs

3.1.1. Mass yield and elemental analysis

The mass yields of torrefied corncobs are shown in Table 2. The yield of torrefied corncobs was affected by torrefaction temperature and residence time. As the torrefaction temperature increased from 250 to 300 °C, the yield of torrefied corncobs decreased gradually from 93.42% to 63.78%. As the residence time of torrefaction increased from 10 to 20 min, the yield of torrefied corncobs dropped from 88.14% to 80.13% and decreased further at longer residence times. The mass loss of corncob during torrefaction was primarily due to the decomposition of hemicellulose and partly because of the depolymerization of cellulose and lignin (Prins et al., 2006a).

The elemental analysis of torrefied corncob is listed in Table 2. It is evident that the carbon content increased significantly with increasing temperature and residence time, whereas the oxygen content decreased. Therefore, the O/C ratio of torrefied corncob decreased with temperature and residence time, suggesting that deoxygenation of corncobs may be the primary reactions during torrefaction. The oxygen of corncobs was likely released mainly in the form of water, and partly as CO, CO_2 and oxygen-containing organic compounds, for instance, methanol, acetic acid and phenols (Prins et al., 2006b; Wang et al., 2011a).

3.1.2. Solid ^{13}C NMR analysis

The solid ^{13}C CP/MAS NMR spectra of torrefied corncob are shown in Fig. 2. Numbered signals corresponding to the different types carbons of the main corncob components (hemicellulose, cellulose and lignin) are tabulated in Table 3. Carbons in hemicellulose, cellulose and lignin represented by numbers and Greek letters are those from the literature (Melkior et al., 2012). The normalized integration values of signals, implying the distributions of different types carbons as percentage of the total carbons in torrefied corncob, are shown in Table 3. The signal at 172.6 ppm is predominantly assigned to the carbonyl carbons of hemicellulose. The carbonyl carbon content decreased from 3.24% to 1.85% while the torrefaction temperature increased from 250 to 300 °C, implying increasing decomposition of hemicellulose in corncobs with elevated torrefaction temperature. The content of carbonyl carbons also decreased with increased residence time of torrefaction. The signals presented at 152.8 ppm are related to the C-3/5 (Carbons in lignin represented by numbers) of etherified syringyl units involved in β-O-4 structures. The content of C-3/5 in etherified syringyls decreased from 0.91% at 250 °C to 0.79% at 275 °C, and then increased to 2.82% at 300 °C. The decrease in etherified syringyl content could either be due to the depolymerization of lignin by cleavage of β-O-4 bonds, or demethoxylation of syringyl units to guaiacyl units (Melkior et al., 2012). The increase of etherified syringyls content at 300 °C might be due to slight decomposition of lignin compared with the severe decomposition and charring of hemicellulose and cellulose. It has been known that the thermal decomposition of hemicellulose and cellulose proceeds faster than that of lignin at a high temperature (Chen et al., 2011; Phanphanich and Mani, 2011). The same variation trends for the signal were observed for the residence time. The signal at 147.9 ppm is associated with the C-3/5 of unetherified syringyl units and C-3/4 of guaiacyl units in lignin. Their content increased gradually with increasing torrefaction temperature, possibly due to charring of the corncobs together with the conversion of etherfied C-3/5 into unetherfied C-3/5 in syringyl units through the cleavage of β-O-4 bonds and transformation of syringyl units into guaiacyl units by demethoxylation. With increasing residence time, the trends in this signal were similar to that with increasing torrefaction temperature.

The signals at 104.9, 74.4 and 72.3 ppm are mainly assigned to C-1/2/3/5 at cellulose. The content of C-1/2/3/5 first changed slightly as the torrefaction temperature was raised from 250 to 275 °C, but decreased significantly at higher temperatures. As the residence time of torrefaction was increased from 10 to 60 min, the contents of C-1/2/3/5 in cellulose also had noticeable dropped. The signals at 88.1, 82.6, 64.4 and 62. 2 ppm are primarily assigned

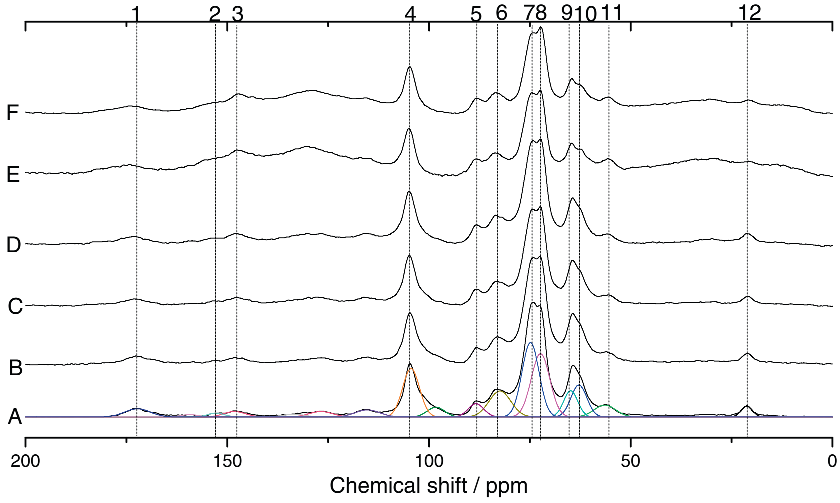

Fig. 2. Solid ^{13}C NMR spectra of torrefied corncob obtained at different torrefaction temperature and residence time. (A) raw corncob, The color line is the deconvolution of spectrum A using Gaussian–Lorentzian fitting. (B) 250 °C, 20 min, (C) 275 °C, 10 min, (D) 275 °C, 20 min, (E) 275 °C, 60 min, (F) 300 °C, 20 min.

Table 2
Mass yield and elemental analysis of torrefied corncob.

Analysis of torrefied corncob		Raw corncob	Residence time: 20 min			Temperature: 275 °C	
			250 °C	275 °C	300 °C	10 min	60 min
Mass yield of torrefied corncob/wt.%		–	93.42	80.13	63.78	88.14	55.35
Elemental analysis/wt.%, daf[a]	C	43.87	45.10	48.54	57.86	47.64	57.33
	H	6.06	6.20	6.65	6.75	6.10	5.93
	O[b]	49.50	48.01	44.06	34.43	45.61	35.92
	N	0.53	0.61	0.70	0.86	0.60	0.75
	S	0.04	0.08	0.05	0.11	0.04	0.06
O/C		1.13	1.06	0.91	0.60	0.96	0.63

[a] daf: Dry ash free basis.
[b] The oxygen content was calculated by difference.

Table 3
The assignment and quantitative analysis of signals in spectra of torrefied corncob.

Signal number	Chemical shift(ppm)	Assignment	Distribution of C as % of total C in torrefied corncob					
			Raw corncob	Residence time: 20 min			Temperature: 275 °C	
				250 °C	275 °C	300 °C	10 min	60 min
1	172.6	Hemicellulose:–$\underline{C}$OO–R,CH_3–$\underline{C}$OO–R	3.64	3.24	2.86	1.85	3.16	1.52
2	152.8	Lignin:S-3(e), S-5(e)	1.16	0.91	0.79	2.82	0.85	3.06
3	147.9	Lignin: S-3(ne), S-5(ne),G-3(ne,e),G-4(ne,e)	2.39	2.79	3.48	7.56	3.03	10.39
4	104.9	Carbohydrates: Cellulose:C-1	12.32	12.40	12.73	7.31	12.15	7.21
5	88.1	Cellulose:C-4(crystalline)	2.54	3.14	4.13	1.83	2.77	1.45
6	82.6	Lignin:Cβ, Cellulose:C-4(amorphous)	10.12	9.06	7.73	4.86	9.14	4.90
7	74.4	Lignin:Cα,Carbonhydrate:C-2/3/5	20.30	19.11	15.78	9.96	16.74	8.93
8	72.3	Carbonhydrate:C-2/3/5	16.44	16.63	15.16	10.01	16.86	9.22
9	64.4	Cellulose:C-6(crystalline)	4.59	4.86	4.97	2.97	4.95	2.77
10	62.2	Lignin:Cγ, Cellulose:C-6(amorphous)	7.91	7.25	6.30	4.67	6.76	4.44
11	56.3	Lignin:–O$\underline{C}$H3	4.24	3.66	3.16	3.92	3.93	3.78
12	21.2	Hemicellulose:–$\underline{C}$H3	2.92	2.63	2.35	0.75	2.48	0.38
	60–106	Carbohydrate carbon	83.61	80.10	69.23	42.42	75.30	39.74
	106–160	Aromatic carbon	9.03	11.48	19.26	30.80	14.41	36.81
Crystallinity (%)			20.06	25.74	34.82	27.35	23.26	22.83

Abbreviations: S, carbon in syringyls (aromatic unit with two methoxyl groups); G, carbon in guaiacyls (aromatic unit with only one methoxyl); ne, in non-etherified arylglycerol β-aryl ethers; e, in etherified arylglycerol β-aryl ethers (Melkior et al., 2012).

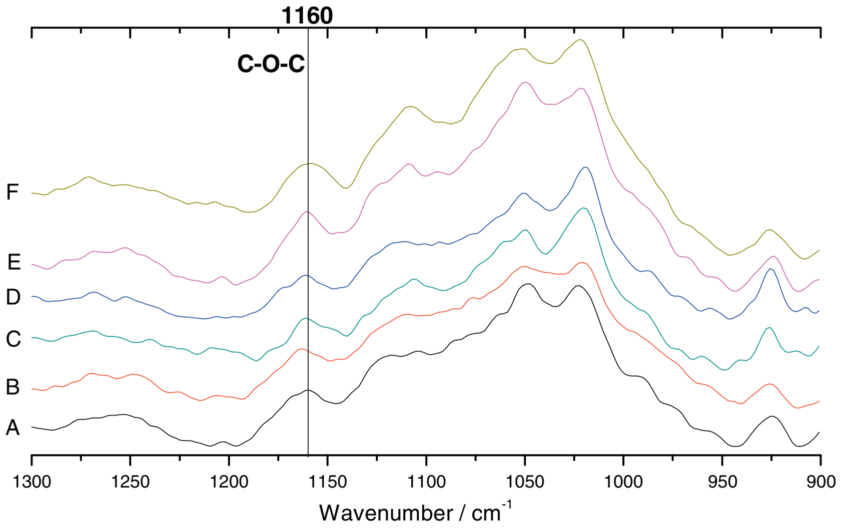

Fig. 3. FTIR spectra of torrefied corncob obtained at different torrefaction temperature and residence time.(A) raw corncob, (B) 250 °C, 20 min, (C) 275 °C, 10 min, (D) 275 °C, 20 min, (E) 275 °C, 60 min, (F) 300 °C, 20 min.

to crystalline C-4, amorphous C-4, crystalline C-6 and amorphous C-6 in cellulose, respectively. The crystalline C-4/6 content first increased slightly as the torrefaction temperature increased from 250 to 275 °C, then dropped drastically as the temperature was increased to 300 °C. At the same time, the amorphous C-4/6 content decreased with increasing torrefaction temperature. The crystallinity of cellulose in corncobs increased first and then decreased with increasing torrefaction severity. The increase in crystallinity of torrefied corncobs could be attributed to the decomposition of hemicellulose and amorphous regions of cellulose. With increasing

Table 4
Product distribution of fast pyrolysis of torrefied corncob.

Products	Yield (wt.%)					
	Raw corncob	Residense time: 20 min			Temperature: 275 °C	
		250 °C	275 °C	300 °C	10 min	60 min
Bio-oil	57.20	55.15	47.60	40.74	50.36	39.35
Char	21.14	24.57	30.21	38.19	26.31	40.70
Non-condensable gas[a]	21.66	20.28	22.19	21.07	23.33	19.95

[a] The yield of non-condensable gas was calculated by difference.

torrefaction severity, decomposition of crystalline cellulose occured, which caused a decrease in crystallinity of the torrefied corncobs. The signal at 56.3 ppm is related to the methoxyl groups of lignin. The content of methoxyl groups first decreased from 3.66% at 240 °C to 3.16% at 275 °C, and then increased to 3.92 at 300 °C. The decrease in methoxyl groups content implies increasing decomposition of lignin. The increase in methoxyl groups at 300 °C could be due to decomposition and charring of hemicellulose and cellulose. The signal at 21 ppm is associated with the methyl carbons of acetyl units in hemicellulose. The content of methyl carbons gradually decreased with increasing torrefaction temperature and residence time.

The spectra obtained at torrefaction conditions of 270 °C, 60 min and 300 °C, 40 min (spectra E and F in Fig. 2) differ markedly from those obtained at lower torrefaction temperatures and shorter residence times. A new broad aromatic signals at 106–110 ppm and aliphatic signals at 0–60 ppm can been observed. In contrast, the signals at 60–105 ppm assigned to carbohydrate carbons decreased drastically. As shown in Table 3, the aromatic carbons content increased from 11.48% at 250 °C to 30.80% at 300 °C while the carbohydrate carbons content decreased from 80.10% at 250 °C to 42.42% at 300 °C. New broad aromatic signals at 106–110 ppm due to an increase in aromatic carbon content indicate charring of hemicellulose, cellulose and lignin at 270 °C, 60 min and 300 °C, 40 min. These results are in accordance with those reported by Melkior et al. (2012).

3.1.3. FTIR analysis of torrefied corncob

The FTIR spectra of torrefied corncob are shown in Fig. 3. One of the noticeable differences in these spectra is the peak area of the signal at 1160 ppm assigned to C–O–C asymmetrical vibration. The higher intensity of the C–O–C vibration with increasing torrefaction severity could be attributed to the formation of cross-linking during cellulose torrefaction. Cross-linking of

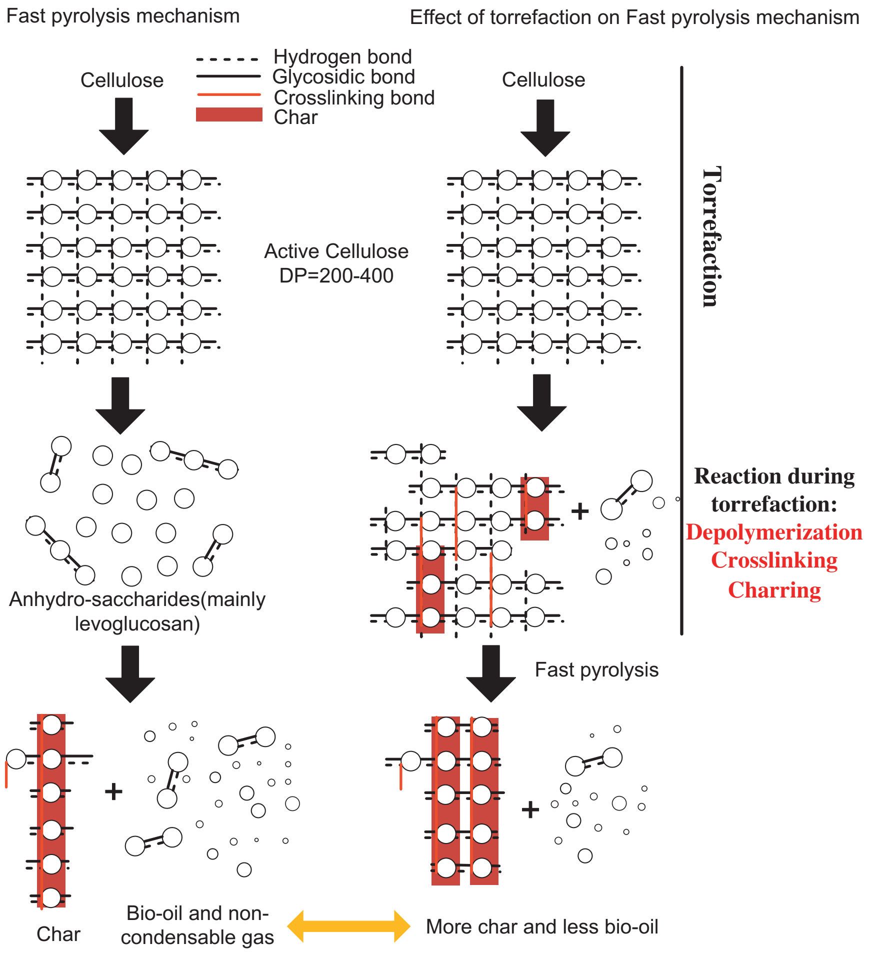

Fig. 4. Effect of torrefaction on fast pyrolysis mechanism of cellulose (Chaiwat et al., 2008).

Table 5
Quantification of Some Compounds in Bio-oil.

Group	RT(min)	Compounds in bio-oil	Composition in bio-oi (wt.%)					
			Raw corncob	Residense time: 20 min			Temperature: 275 °C	
				250 °C	275 °C	300 °C	10 min	60 min
Acids	10.46	Acetic acid	6.85	6.03	5.19	4.23	6.27	3.33
	12.53	Propanoic acid	0.31	0.36	0.46	0.52	0.64	0.41
	Total		7.16	6.40	5.65	4.75	6.91	3.74
Ketones	7.54	Hydroxyacetone	4.81	3.96	3.40	2.26	2.44	1.78
	8.63	2-Pentanone, 4-hydroxy-4-methyl-	0.96	0.95	1.01	0.99	1.04	0.79
	8.54	2-Cyclopenten-1-one	0.58	0.70	0.87	0.85	0.75	0.60
	8.89	1-Hydroxy-2-butanone	0.64	0.71	0.64	0.44	0.61	0.22
	11.96	2-Cyclopenten-1-one, 3-methyl-	0.35	0.44	0.56	0.56	0.48	0.36
	12.43	2-Cyclopenten-1-one, 2,3-dimethyl-	0.09	0.12	0.17	0.21	0.17	0.12
	17.32	1,2-Cyclopentanedione	0.24	0.22	0.12	0.17	0.10	0.06
	18.28	1,2-Cyclopentanedione, 3-methyl-	0.50	0.64	0.64	0.54	0.42	0.34
	Total		8.16	7.73	7.42	6.02	6.01	4.26
Furans	10.84	Furfural	0.76	0.68	0.57	0.42	0.67	0.18
	15.32	2-Furanmethanol	0.10	0.12	0.09	0.21	0.23	0.12
	26.53	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	0.12	0.14	0.14	0.13	0.09	0.10
	Total		0.98	0.94	0.80	0.76	0.99	0.40
Phenols	18.82	Phenol, 2-methoxy-	0.22	0.35	0.40	0.44	0.40	0.28
	20.23	Phenol, 2-methoxy-4-methyl-	0.03	0.14	0.13	0.14	0.19	0.18
	22.04	Phenol, 3-methyl-	0.06	0.11	0.18	0.27	0.18	0.15
	20.94	Phenol	0.50	0.61	1.11	1.42	1.15	0.99
	21.24	Phenol, 4-ethyl-2-methoxy-	0.07	0.18	0.23	0.28	0.31	0.16
	21.93	Phenol, 4-methyl-	0.06	0.11	0.27	0.40	0.29	0.24
	23.08	Phenol, 4-ethyl-	0.00	0.28	0.49	0.60	0.57	0.31
	23.34	2-Methoxy-4-vinylphenol	0.00	0.47	0.38	0.40	0.27	0.09
	25.07	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	0.20	0.07	0.09	0.08	0.16	0.17
	24.11	Phenol, 2,6-dimethoxy-	0.34	0.20	0.27	0.36	0.18	0.14
	25.57	Benzofuran, 2,3-dihydro-	0.02	0.71	0.59	0.53	0.28	0.07
	27.37	Vanillin	0.13	0.11	0.07	0.06	0.11	0.08
	29.32	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.58	0.08	0.08	0.08	0.07	0.01
	29.01	1,2-Benzenediol	0.11	0.18	0.22	0.21	0.14	0.20
	Total		2.45	3.60	4.51	5.27	4.30	3.07

Table 6
Physical properties of bio-oil.

Physical properties of bio-oil	Raw corncob	Residence time: 20 min			Temperature: 275 °C	
		250 °C	275 °C	300 °C	10 min	60 min
Water content	35	33	25	21	30	22
High heating value MJ/kg	14.85	15.12	16.49	17.21	15.58	17.09
pH	2.68	2.97	3.30	3.34	2.88	3.35
Kinematic viscosity at 20 °C/cSt	3.42	3.96	7.27	12.62	4.23	12.48

cellulose is probably a bimolecular nucleophilic substitution reaction in which a hydroxyl group of one cellulose chain is protonated first, then the protonated hydroxyl group is attacked by a second cellulose chain as a nucleophile to form ethers and water (Molton and Demmitt, 1977; Scheirs et al., 2001).

3.2. Effect of torrefaction on bio-oil characteristics

3.2.1. Product distribution from fast pyrolysis of torrefied corncob

The product distribution from fast pyrolysis of torrefied corncob is shown in Table 4. Elevated torrefaction temperatures improved the yield of char and decreased the yield of bio-oil. The maximum yield of bio-oil was obtained with raw corncob. Similar trends were observed with increasing residence times. These results could be explained by a less decomposition of lignin compared with that of hemicellulose and cellulose. Simultaneously, carbonization of hemicellulose, lignin, and especially the cellulose occured. According to the experimental results and those reported in the literature (Chaiwat et al., 2008; Kawamoto et al., 2003; Lin et al., 2009; Shen and Gu, 2009; Shen et al., 2010), the effect of torrefaction on fast pyrolysis of cellulose was proposed in Fig. 4. The left of the figure shows a simplified fast pyrolysis mechanism of cellulose. Cellulose first forms active cellulose with a degree of polymerization (DP) of 200–400. Active cellulose then decomposes to produce anhydrosaccharides (mainly levoglucosan). The levoglucosan can further undergo parallel pathways to form char, bio-oil and no-condensable gas. The right of Fig. 4 shows the effect of torrefaction on fast pyrolysis. During torrefaction, cellulose first depolymerizes to form active cellulose species, then the active cellulose undergoes crosslinking. The crosslinked cellulose can further undergo polycondensation to form char. In fast pyrolysis, The crosslinking and charring of cellulose predominantly produce char, which results in a higher char yield and lower bio-oil yield at increasing torrefaction temperature and residence time.

3.2.2. Quantification of some compounds in bio-oil

Several compounds in bio-oil were selected for quantitive analysis by GC–MS due to their high relative peak areas. The chemical compounds are mainly carboxylic acids, furans, ketones and phenols (Table 5). The acetic acid content decreased moderately with increasing torrefaction temperature and residence time. A maximum acetic acid content of 6.85% was achieved with raw corncob, whereas the lowest value of 3.33% was obtained from corncob torrefied at 275 °C and a residence time of 60 min. The furfural content also decreased gradually with torrefaction temperature and residence time. The two compounds are mainly derived from hemicellulose and cellulose pyrolysis (Zheng et al., 2012). The results could have been caused by the decrease and charring of hemicellulose and cellulose in torrefied corncobs with increasing torrefaction severity. Most of the phenolic compounds including 2-methoxyphenol, 3-methylphenol, phenol, 4-ethyl-2-methoxyphenol, and 4-ethylphenol, which primarily derived from lignin depolymerization, increased with elevated torrefaction temperature, likely due to increased lignin content in corncobs torrefied at elevated temperature. With increasing residence time from 10 to 20 min, the phenolics content also increased. The phenolics content decreased when the residence time increased from 20 to 60 min, possibly due to severe charring of the corncobs during torrefaction at long residence times.

3.2.3. Physical properties of bio-oil

The physical properties of bio-oil are shown in Table 6. The water content decreased from 35% to 21% with elevated torrefaction severity, likely due to drying and dehydration reactions during torrefaction. The high heating value and kinematic viscosity of bio-oil increased with elevated torrefaction, possibly caused by a decreased water content and increased lignin-derived compounds, i.e. pyrolytic lignin (Garcia-Perez et al., 2008a). The pH of bio-oil increased slightly with torrefaction severity, paralleling a decrease in acetic acid content in bio-oil.

4. Conclusion

Torrefaction can serve as thermal pretreatment prior to fast pyrolysis for improving the quality of bio-oil. Heating value and pH of bio-oil increased with elevated torrefaction severity, whereas the yield of bio-oil decreased significantly. The decrease of bio-oil yield was attributed to the crosslinking and charring of corncobs during torrefaction. The factors affecting crosslinking and charring of biomass include torrefaction temperature, residence time and heating rate. Hence, in order to limit crosslinking and charring, torrefaction using microwave reactor in low temperature or torrefaction using heat carrier (e.g. silica sand) for high heating rate and short residence time is preferred in next study.

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